The enhanced uranyl-amidoxime binding by the electron donating substituents

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Contents

1. Materials and sample preparation

HPLC grade methanol was obtained from Fisher Scienctific (Pittsburgh, PA, USA). Deionized water was prepared by the Milli-Q system (Millipore, Bedford, MA, USA). The uranyl nitrate was purchased from China National Nuclear Coorperation (Beijing, China). All the amidoxime ligands were systhesized using the previously reported routine.

All the samples were dissolved in deionized water at the concentration of 0.01 M as the stock solution. They were diluted with before the experiments using the corresponding solvents (see below).

2. Mass spectrometry instrumental parameters

All the MS experiments were performed on the LTQ-XL linear ion trap mass spectrometer (Thermo Fisher, San Jose, USA). The electrospray ionization (ESI) ion source was operated in positive ion mode. The sample solutions were infused into the instrument at the flow rate of 5 μL min^{-1}. Under the balance of the surface tension and the applied electric field, Taylor cone was formed and the end of solution flow. During a series of Column fission, the primary droplets generated at the Taylor cone decomposed into progeny droplets with the assistance of the nebulizer gas. Ultimately, the sample molecules were ionized, mass selected, and detected by the MS instrument.

The optimized instrumental parameters included: spray voltage of 3.5 kV, nebulizer gas pressure of 5 arbitrary units, cone voltage of 40 V, tube lens offset of 60 V, and the temperature of the transporting capillary of 300 °C. In tandem MS, the selected ions were isolated in the ion trap, and subjected with normalized collision energy (NCE) by collision with the buffer gas (He) in the trap. The MS data was processed with the manufacturer software (Xcalibure 2.2).

3. Fluorescence quenching experiments

The fluorescence experiments were performed on the LS-55 Lumina Fluorescence Spectrometer (Thermo Scientific). The acidity of the solutions (pH=7.0) was adjusted by MES buffer (0.05 M). Under this condition, the maximum emission of uranyl was observed around 530 nm with the excitation light of 380 nm (Fig. S1). For the quenching experiments, the fluorescence of the solutions contained 0.1 mM uranyl and different equivalents (0.1, 0.5, 1.0, 2.0, 4.0, and 6.0) AO ligands were recorded, respectively. The quenching profiles were calculated and plotted by the Stern-Volmer equation. The conditional stability constants (logK$_{SV}$) were obtained from the slopes of the plots.
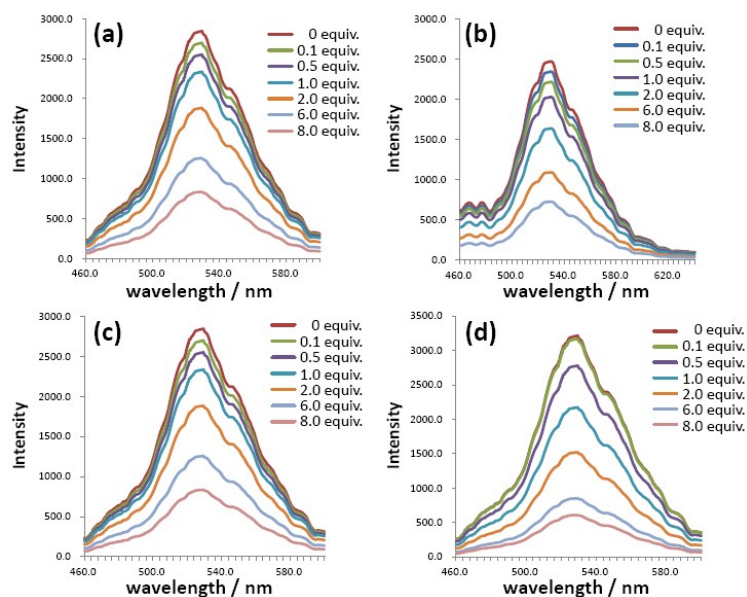
Fig. S1. The fluorescence spectra of uranyl with (a) AO1, (b) AO2, (c) AO3, and (d) AO4 ligands.

4. Vibrational spectroscopy

The Raman spectra were obtained on the LabRAM XploRA spectrometer (Horiba Scientific), and the IR spectra were obtained on the Bruker Vertex 70 FT-IR spectrometer with Attenuated Total Reflection (ATR) accessary and MCT (mercury cadmium telluride) detector. The Raman and IR spectra of uranyl with different AO ligands were shown in Fig. S2 and Fig. S3.

In the Raman spectra (Fig. S2), the symmetric stretching band (v_1) shifted from 866 cm^{-1} to around 830 cm^{-1} for AO1, AO2, AO3, and AO4. The location of these bands, however, was the same for these ligands. For AO5 with the strong electron withdrawing group (-NO$_2$), its vibration band was similar to that of uranyl, indicating the much poorer binding between them. The IR spectra of uranyl with the AO ligands were shown in Fig. S3. Similarly, the location of the asymmetric stretch bands of uranyl presented little difference upon the addition of the AO ligands.
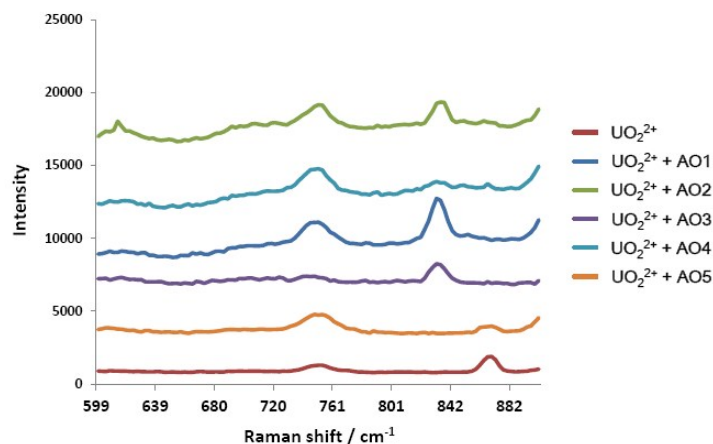

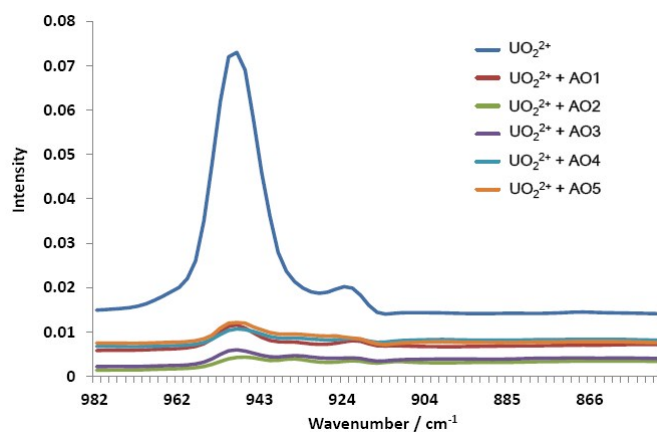Fig. S2. The Raman spectra of uranyl (0.01 M) with AO ligands (0.01 M).

Fig. S3. The Raman spectra of uranyl (0.01 M) with AO ligands (0.01 M).

5. Density functional theory (DFT) calculations

All the DFT calculations were performed with Gaussian 09 package.[2] The computation conditions for the geometry optimization are the same with those in our previously report. Briefly, the B3LYP functional was utilized. The Stuttgart/Dresden's small core (SC) relativistic effective core pseudo potential (RECPs) utilizing the Wood-Boring quasi-relativistic was used for U atom,[3] and the total electron 6-311G (d, p) basis set was used for C, H, O and N atoms. Frequencies at the same level have been checked to confirm that the optimized geometries are at the local minima on the potential energy surfaces.

References

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